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Effect of Exocyclic Substituents and π-System Length on the Electronic Structure of Chichibabin Diradical(oid)s

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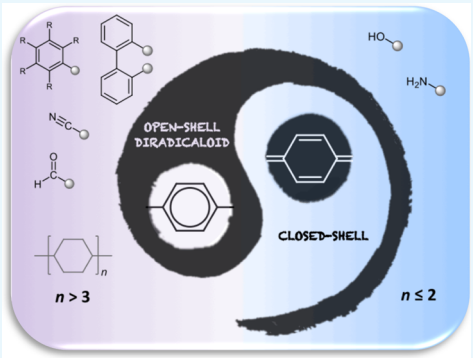
Supporting Information

ABSTRACT: The ground state (GS) of Chichibabin's polycyclic hydrocarbons (CPHs) can be singlet [open- or closed-shell (OSS or CS)] or triplet (T), depending on the elongation of the π-system and the exocyclic substituents. CPHs with either a small singlet−triplet energy gap (ΔE_{ST}) or even a triplet GS have potential applications in optoelectronics. To analyze the effect of the size and exocyclic substituents on the nature of the GS of CPHs, we have selected a number of them with different substituents in the exocyclic carbon atoms and different ring chain lengths. The OPBE/cc-pVTZ level of theory was used for the optimization of the systems. The aromaticity of the resulting electronic structures was evaluated with HOMA, NICS, FLU, PDI, I_{ring}, and MCI aromaticity indices. Our results show that the shortest π-systems (one or two rings) have a singlet GS. However, systems with three to five rings favor OSS GSs. Electron-withdrawing groups (EWGs) and aromatic substituents in the exocyclic carbons tend to stabilize the OSS and T states, whereas electron-donating groups slightly destabilize them. For CS, OSS, and T states, aromaticity measures indicate a gain of aromaticity of the 6-membered rings of the CPHs with the increase in their size and when CPHs incorporate EWGs or aromatic substituents. In general, the CPHs analyzed present small singlet−triplet energy gaps, and in particular, the ones containing EWGs or aromatic substituents present the smallest singlet−triplet energy gaps.



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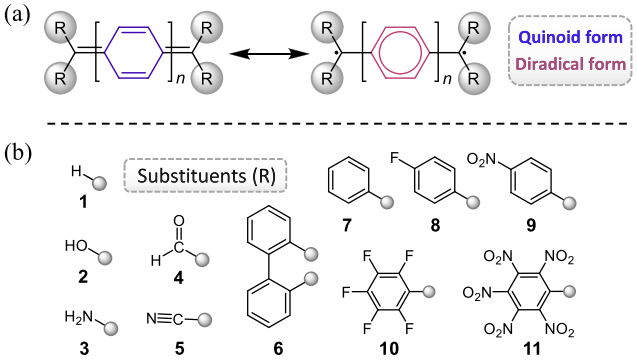
INTRODUCTION

Chichibabin's polycyclic hydrocarbon (CPH), *p,p'*-biphenylene-bis-(diphenylmethyl) (n = 2 and R = Ph in Scheme 1a), was synthesized in 1907[1] by Russian chemist Aleksei Yevgen'evich Chichibabin.[2] Three years before, Thiele and Balhorn[3] reported an analogue hydrocarbon with n = 1 and R = Ph, whereas Müller and Pfanz[4] produced the species with n = 3 and R = Ph in 1941. The electronic structure of Chichibabin's compounds and that of their derivatives (closed-shell quinoid vs open-shell diradical forms, Scheme 1a) have been a recurring topic of debate for both theoretical and experimental chemists.[5] In 1986, despite the extremely oxygen-sensitive nature of Chichibabin's hydrocarbon, Montgomery et al.[6] determined its molecular structure by X-ray diffraction. In addition, they determined that this molecule has a singlet ground state (GS) with a small singlet−triplet energy gap (ΔE_{ST}) and a large amount of diradical character, i.e., it is a Kekulé diradicaloid. Chichibabin's, Müller's, and related hydrocarbons have usually a diradical or diradicaloid GS and a small ΔE_{ST}.[6−8] These species are getting special attention owing to the tunable character of their GS that can be singlet [open- (OSS) or closed-shell (CS)] or triplet (T), depending on the length of the π-system and the exocyclic substituents.[9−11] In general, the longer the hydrocarbon, the greater the diradical character.[12] Indeed, many investigations support this relationship and also add the fact that the aromaticity is increased in larger CPH systems.[13,14]

π-Conjugated open-shell diradical(oid)s, such as Chichibabin's and Müller's hydrocarbons and analogues, are being intensively investigated as potentially multiple functional organic materials that can be employed as semiconductors in

Scheme 1. (a) Quinoid and Diradical (Benzoid) Resonance Forms of CPHs; (b) Different Substituents Studied in This Work



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organic field effect transistors,[15,16] as organic light-emitting diodes,[17] as light-harvesting dyes in organic solar cells,[18] as near-infrared fluorescent probes,[19] and as chromophores in nonlinear optics (NLO).[11,20−22] Indeed, NLO properties were shown to be particularly enhanced for systems having intermediate diradical character such as Chichibabin's hydrocarbons.[23−26] Unfortunately, the intrinsic instability of these hydrocarbons prevents their practical applications. For this reason, several related hydrocarbons with increased stability have been synthesized in the last decade.[12,27−36] The quest of thermally stable diradicals arouses considerable interest because these molecules have a great potential for numerous advance applications.[37]

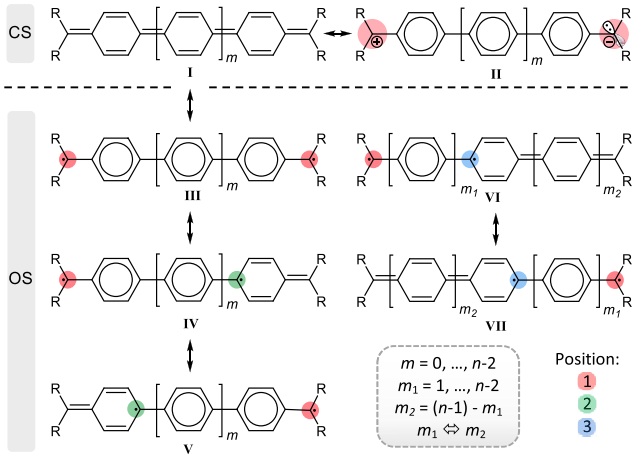
It has been recently shown that substituents on the two biphenylmethylene moieties of tetrabenzo-Chichibabin's hydrocarbons have a significant influence on their chemical bonding and physical properties.[38] From a computational point of view, studies regarding the effect of the substituents on the molecular structure of CPHs or other oligothiophenes analogues are limited to few examples. Most of the studies are mainly focused on the effect of the CPH chain elongation.[26,39] For the case of quinoidal thiophene oligomers, Nakano and coworkers[26,40] examined the effect of the substituent at the terminal positions, by replacing R = H by CN, showing that the effect of this replacement is small. The main aim of this work is to study what is the effect of the exocyclic substitution in Chichibabin's hydrocarbons on their stability and diradical character. We will also analyze the influence of the length of the π-system. In particular, we will consider Chichibabin's hydrocarbons with n in the range of 1−5 and as substituents the set depicted in Scheme 1b. Some of the substituents have π-donor character (**2**, **3**), others have π-acceptor character (**4**, **5**), and some of them have aromatic rings with more or less π-acceptor or π-donor character (**6** to **11**). Our hope is that the results obtained provide clues that will help designing polycyclic hydrocarbons with enhanced stability and tuned diradical character.

■ RESULTS AND DISCUSSION

Geometry optimizations of different CPHs, with substituents from **1** to **11** (Scheme 1) and chain lengths (n) from 1 to 5 rings (to refer to a specific compound, we will employ the nomenclature: substituent$_n$), were performed at the OPBE/cc-pVTZ level of theory. Three electronic states, namely, closed-shell singlet (CS), open-shell singlet (OSS), and triplet (T), were considered for the calculations. Scheme 2 represents the resonance structures proposed for the $n \geq 2$ systems, which can present from 0 to n aromatic π-sextets.[41,42]

Data in Table 1 show that for $\mathbf{7}_1$ and $\mathbf{7}_2$, for which experimental X-ray data is available,[6] the theoretical bond distances are in good agreement with the experimental ones if one considers that the GS of these CPHs is the CS, as experimentally found.[6] From all optimized geometries, only the CS systems **1**, **2**, and **3** with $n \leq 2$ are planar (dihedral angle values (α) lower than 5°), indicating a huge contribution of the quinoid resonant form in these cases. For the $n = 2$ geometries, the H···H distance between neighbor hydrogens of the chain rings is about 1.95 Å, less than the sum of their van der Waals radii. In spite of this, the molecule is planar because the stabilizing effect of the conjugation is strong enough to outweigh the H···H repulsion. However, in other systems with $n \leq 2$, the α values can be up to 22° (**6**), indicating a diminished quinoid contribution to the CS structure in this

Scheme 2. Proposed Resonance Forms for the CS (Top) and OSS/T (Bottom) States of the Chichibabin Polycyclic Hydrocarbons[a]



[a]The different radical positions represented for the OSS/T case are also possible for the equivalent CS situation with zwitterionic structure (for instance, structure **III** is the radical analogue of **II**; there are zwitterionic structures analogues of **IV** to **VII**). n represents the total number of rings.

short-ring-chain cases. Most of these CPHs are nonplanar because of the twisting distortion of the 6-membered rings. The dihedral angle that measures this distortion can be either positive or negative. Because of that, we have a number of possible conformers (see Figure S3). We analyzed all possible conformers for $\mathbf{1}_n$ (n = 2 to 5), and our results showed that energy differences between conformers are not larger than 0.003 eV (see Table S2). For this reason, for the rest of the systems, we decided to start the optimization from the planar geometry and to use the final geometry without analyzing whether it corresponds to the most stable conformer. As can be seen from the α values (Table 1), the loss of planarity is smaller in the case of CS than in OSS and T structures, but even so, the distortion in the CS case is still significant. This loss of planarity is also increased by enlarging the chain length. In systems having more neighbor H pairs, the repulsive contribution become more important; for example, in the case of system **1** having $n = 3$ (so, two nonbonded H pairs), α values are around 14°, whereas for $n = 5$ (four H pairs), the α values range from 25 to 32°. H···H repulsions decrease with torsion at the cost of reducing conjugation. The degree of distortion is also affected by the nature of the R group; an electron-donating group (EDG) (**3**) presents smaller α values than EWG and aromatic substituents (**5**, **6**, and **7**). This can be related to the fact that EDGs are not efficient in stabilizing the negatively charged C atom (structure **II** and zwitterionic analogues of **IV** to **VII**), thus disfavoring the benzoid forms.

As said before, the twisting distortion is larger in OSS and T states. For these states, the inter-ring C−C bond is a single bond and, therefore, rotation over this bond is easier than in the CS states. For the T states, α is always larger than 35°. This situation reminds that of the biphenyl system that is distorted by 44.4°[43] to avoid steric hindrance with ortho hydrogen atoms.[44] For these systems, there is an interplay between the gain of stabilization due to conjugation in the planar geometry and the reduction of H···H repulsions for α = 90°. The actual dihedral angle represents the best compromise between these two counteracting forces for each case. EDG (**3**) presents

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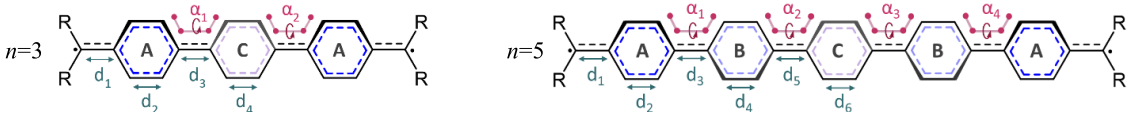
Table 1. Selected Bond Distances (Å), Angles (°), and Harmonic Oscillator Model of Aromaticity (HOMA)[a] Values (au) Calculated (OPBE/cc-pVTZ) for 1, 3, 5, 6, and 7 Chichibabin Systems in Closed- and Open-Shell Singlet and Triplet States



system$_n$	state	d_1	d_2	d_3	d_4	d_5	d_6	α_1[b]	α_2[b]	α_3[b]	α_4[b]	HOMA$_A$	HOMA$_B$	HOMA$_C$
1$_3$	CS	1.373	1.365	1.433	1.372			13.7	13.7			0.576		0.755
	OSS	1.393	1.375	1.460	1.383			28.7	28.7			0.773		0.910
	T	1.401	1.379	1.472	1.387			36.9	36.9			0.833		0.948
1$_5$	CS	1.381	1.371	1.455	1.382	1.465	1.384	25.0	30.8	31.5	26.1	0.697	0.911	0.928
	OSS	1.399	1.378	1.470	1.387	1.476	1.388	34.8	38.9	39.7	35.3	0.822	0.951	0.957
	T	1.399	1.378	1.470	1.387	1.476	1.388	34.9	40.0	40.0	34.9	0.823	0.950	0.959
3$_5$	CS	1.409	1.374	1.453	1.382	1.463	1.384	22.4	28.8	29.5	23.2	0.752	0.899	0.918
	OSS	1.413	1.377	1.463	1.386	1.473	1.387	29.1	36.3	36.7	29.5	0.793	0.935	0.949
	T	1.414	1.377	1.464	1.386	1.474	1.388	29.9	37.4	37.8	30.1	0.796	0.938	0.952
5$_5$	CS	1.427	1.376	1.461	1.383	1.468	1.385	30.3	33.8	32.9	29.1	0.844	0.926	0.936
	OSS	1.435	1.379	1.469	1.386	1.475	1.387	35.0	39.2	38.4	34.3	0.871	0.948	0.956
	T	1.435	1.379	1.469	1.386	1.475	1.388	35.2	39.6	38.9	34.7	0.883	0.949	0.957
6$_5$	CS	1.446	1.384	1.472	1.387	1.475	1.388	36.2	38.5	38.6	37.6	0.915	0.953	0.955
	OSS	1.454	1.386	1.475	1.388	1.477	1.388	39.0	40.5	40.4	39.7	0.936	0.959	0.960
	T	1.454	1.386	1.475	1.388	1.477	1.388	39.0	40.5	40.4	39.7	0.936	0.959	0.960
7$_1$	X-ray[c]	1.381	1.346											
	CS	1.397	1.361									0.445		
	T	1.467	1.386									0.918		
7$_2$	X-ray[c]	1.415	1.371	1.448										
	CS	1.411	1.369	1.431				16.0				0.668		
	T	1.456	1.385	1.474				38.0				0.918		

[a]HOMA indices computed using the ESI-3D program. [b]The dihedral angle results are in absolute values. [c]X-ray values for the **7** compound with n = 2 from ref 6. See the Supporting Information (SI) for other systems results.

smaller α values than EWG and aromatic substituents (**5**, **6**, and **7**), as expected from the fact that EWGs and aromatic substituents can better stabilize the radical centers, thus favoring the benzoid forms.

Similar arguments can be applied to explain the bond distances and harmonic oscillator model of aromaticity (HOMA)[45−47] values. In the previously discussed cases, where the benzoid form is preferred, outer-ring bonds (d_1, d_3, and d_5) are larger and inner-ring bonds (d_2, d_4, and d_6) are closer to the aromatic C−C distance (1.40 Å). HOMA indices are closer to 1 in these cases (an aromatic compound has an HOMA value close to 1, whereas a nonaromatic has value 0 or even lower). Moreover, we can observe that both bond distances and HOMA values are indicating that central rings (C and B) are more aromatic than the external ones (A). This is in good agreement with the existence of the proposed resonant forms (Scheme 2) since in most of the structures the aromatic sextet is maintained in the central rings but not in the external ones. Interestingly, HOMA values in between 0.5 and 0.7 are calculated for CPHs in their CS states, indicating a partial aromatic character of the 6-membered rings that reveals the importance of resonance structure **II** and analogues.

To gain deeper insight into the electronic structure of the Chichibabin diradical(oid)s (OSS and T states), we analyzed the Mulliken spin densities of those carbons contained in the main axis of symmetry of the molecule (see Tables S20−S30 of the SI for more details). We observe that in systems with small n values the spin densities of carbons in position 1 are close to 1 (or −1), whereas the other carbon atoms have values close to 0. By increasing n, the spin population values decrease in position 1 carbons and increase in position 2 carbons; for example, in the R = H and n = 4 system, the populations of positions 1 and 2 are 0.7 and 0.2, respectively. Alternatively, in all cases, we have found values close to 0 for the position 3 carbons, indicating that the resonance forms with radicals in these positions are not particularly relevant for describing the OSS and T state structures.

The energies (ΔE_{CS-X}, where X = OSS or T) estimated by means of quantum chemical calculations, in most of the cases, suggest that the GS is a CS state for species with $n \leq 2$ and an OSS state for larger n compounds, having a situation like the one depicted in Figure 1 for species **8**. For systems with diradical character, we would expect a T GS according to the Hund rule. However, we found that even though the T state lies close to the OSS singlet, it is always higher in energy.[48,49]

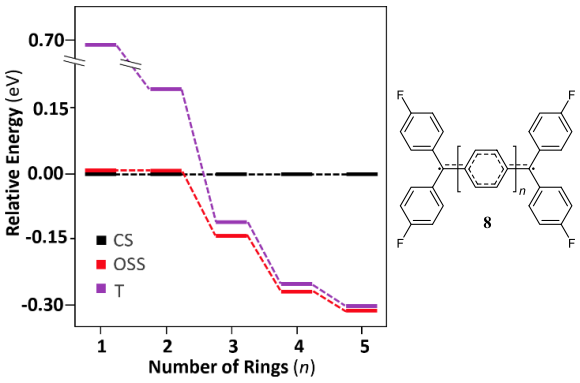


Figure 1. Energy (eV) diagram of the CS, OSS, and T states (referred to CS) depending on n for the R = p-fluorobenzene system (**8**).

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This fact can be explained by the two-state model of Zilberg and Haas.[50] They attribute the extra stabilization of the OSS to the possible resonance structures that can exist in the OSS but not in the T form. Since in the T state, the parallel unpaired electrons cannot form a bond, some of the resonance structures are excluded.

Among all systems, there are three exceptions. The first one is system **3**, having a CS GS for n = 1−3 (Table 2). Then, systems **6** and **11**, in which for n = 1 the GS is also CS, but in the case of n = 2, the OSS solution lies 60.59 and 2.59 meV, respectively, below the CS state. When the OSS solution is lower in energy than the CS, the CS solution can be considered a singlet excited state. In the case of T states, the general trends for the relative energies (with respect to the CS state) are dependent on the substituent nature in a manner similar to the OSS results for n > 2. As regards to EDG (**2** and **3**), T state lies above the CS up to n = 3. In the case of **6** and **11**, only the T state of n = 1 system is higher in energy than the CS, and in the remaining cases, H (**1**), EWG (**4** and **5**) and aromatic (**7**, **8**, **9**, and **10**) substituents, the T is less stable than the CS state for n up to 2. Interestingly, for compounds **6** and **11** with $n \geq 3$, the OSS and T states are much more stable than the CS. Especially, remarkable is the case of $\mathbf{11}_3$ and $\mathbf{11}_4$ where the OSS solution is more than 0.40 eV more stable than the CS one. Our study provides evidence that the exocyclic substituents have a direct effect on the nature of the GS of Chichibabin's systems. EDGs favor the CS form, whereas EWGs and aromatic groups stabilize the diradical form, consequently favoring the OSS and T situations. Our calculations indicate that $\mathbf{1}_3$, $\mathbf{4}_3$, $\mathbf{5}_3$, and $\mathbf{6}_2$ systems have almost degenerated CS and T states (with energy differences not larger than 0.03 eV), whereas almost all systems with n = 5 together with $\mathbf{11}_3$ and $\mathbf{11}_4$ have particularly stable diradical GS.

Table 2. Summary of the Calculated Relative Energies (meV) Referred to the CS State for OSS and T States of n = 2 and n = 3 Systems[a]

	n = 2		n = 3		
system	OSS	T	OSS	T	y
1	0.00	437.86	−93.82	−24.25	0.31
2	0.00	541.91	−20.00	98.42	0.07
3	0.00	608.17	−0.04	187.39	0.00
4	0.00	155.80	−72.36	−17.44	0.38
5	0.00	272.09	−78.53	−20.32	0.26
6	−60.59	−18.05	−192.30	−186.26	0.73
7	0.00	188.66	−139.32	−118.51	0.53
8	0.00	193.22	−133.72	−112.34	0.52
9	0.00	123.74	−133.37	−123.42	0.57
10	0.00	278.99	−107.44	−71.40	0.42
11	−2.59	130.68	−455.30	−428.07	0.41

[a]For n = 3, the diradical character (y) of the OSS systems is also included.

For all compounds, we observe a decrease of ΔE_{ST} when n is increased until reaching the degeneracy of the states (Figure 2). This is because at high n values the distance between radical centers increases, and hence, the energy difference between OSS and T states is reduced. There is a clear trend regarding the effect of increasing the chain length, that is the lowering of the singlet−triplet gap with the increasing number of n. Therefore, for small n values, we have CS CPHs; for larger n, CPHs are diradicals; and for intermediate n values,

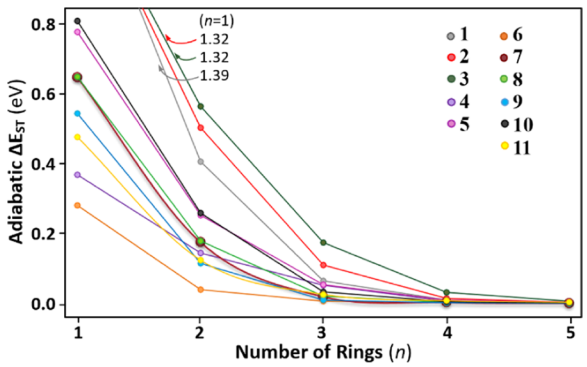

Figure 2. Adiabatic ΔE_{ST} (where S is the lowest singlet state, which can be CS or OS) against the number of rings, for R groups **1**−**11**.

CPHs are diradicaloids,[9] the borders between the different species being somewhat fuzzy and R dependent. This is corroborated by the increase of y values (see Computational Details) from 0 (CS species) to 1 (pure diradical) going from n = 1 to 5 (Table S19). Moreover, y is also affected by the exocyclic substituents (Table 2b), and the results are consistent with the structural and energetic measures. Systems $\mathbf{2}_3$ and $\mathbf{3}_3$ present CS character, whereas the others are diradicaloids with y values from 0.3 to 0.7, with the aromatic groups being the ones presenting larger y values. Finally, the trends in ΔE_{ST} value differ for small and large systems. For small n values (CS ground state), one can notice that there is a significant difference between the two EWG systems **4** and **5**. In the case of n = 1 and 2, the singlet−triplet energy gap for **5**, which has a large electron-accepting character, is larger than for **4**. On the other hand, for the case of EDG, there are no differences between both EDG **3** and **4**. For n > 2 (OSS ground state), ΔE_{ST} is almost the same for the two EWG **4** and **5** (see Figure 2), whereas for the two EDG **2** and **3**, there are some differences, ΔE_{ST} being somewhat larger for **3** having the substituent with higher π-donor character (R = NH_2).

We performed an exhaustive evaluation of the aromaticity using many electronic indices, MCI, PDI, I_{ring}, and FLU; magnetic $NICS(0)_{zz}$ and $NICS(1)_{zz}$ indices; and the previously commented geometric index, HOMA. In the case of MCI, PDI, and I_{ring}, positive values close to the result obtained for benzene are indicative of the aromatic character of the analyzed rings, whereas smaller values close to those of cyclohexane correspond to nonaromatic species (Table 3). In the case of FLU, the maximum aromaticity is achieved when FLU = 0. Finally, for the nucleus-independent chemical shift (NICS), negative values indicate that the compound is aromatic, and vice versa.

The trends of aromaticity values given by the different indices correlated with the CS-T energy gaps for compounds **1**, **3**, **5**, and **6** (one substituent belonging to one of the four different groups studied) are presented in Figure 3. In general, we can observe a good agreement between the different indices, showing the following orders from less to more aromatic: **1** < **3** < **5** < **6** in the CS singlet and **3** < **1** < **5** < **6** in the T state, with an exception in the case of NICS, which classifies **3** as the less aromatic compound in both cases, CS and T. For the **1**, **3**, and **5** CS structures, the values obtained resemble those of the nonaromatic cyclohexane and 1,4-cyclohexadiene results. Instead, for most of the T and some of the **6** CS forms, the results are more similar to those of benzene. ΔE_{ST} is small when the difference between the

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Table 3. Aromaticity Indices of Reference Systems (Benzene, 1,4-Cyclohexadiene, and Cyclohexane) Calculated at the OPBE/cc-pVTZ Level of Theory

	MCI	PDI	I_{ring}	FLU	$NICS(0)_{zz}$	$NICS(1)_{zz}$
benzene	0.073	0.106	0.049	0.000	−15.2	−29.3
1,4-cyclohexadiene	0.002	0.020	0.002	0.073	26.1	4.4
cyclohexane	0.000	0.010	0.000	0.088	23.3	3.5

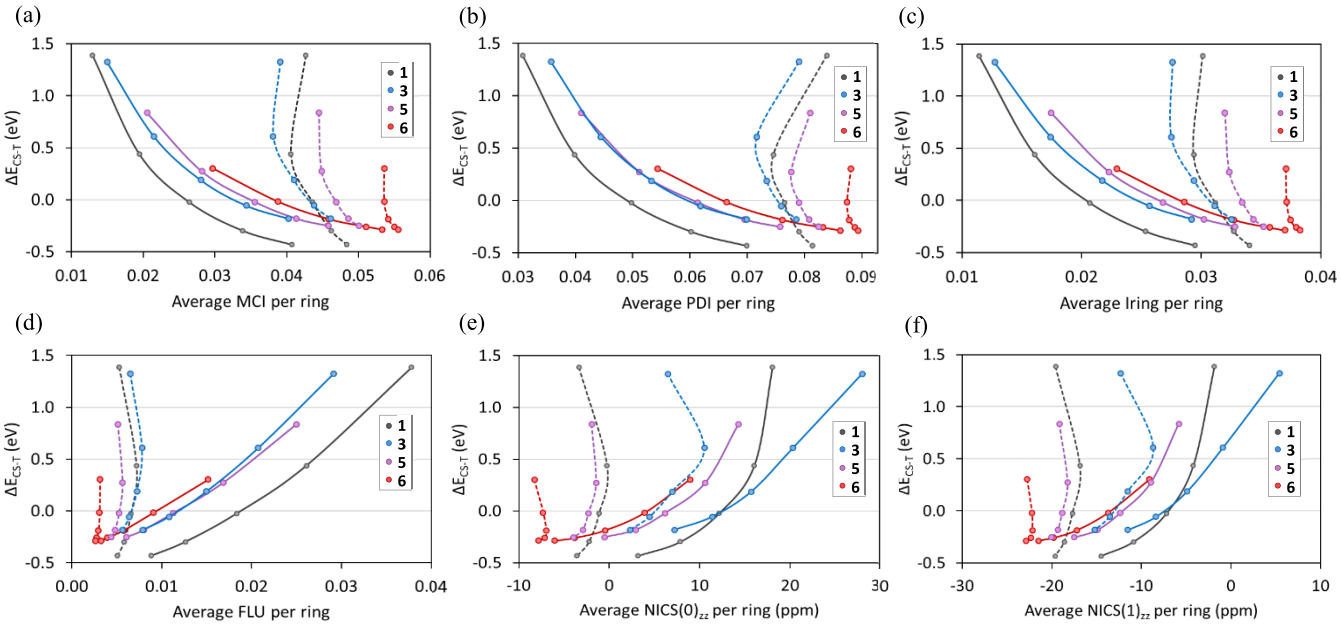

Figure 3. Singlet (CS)−triplet energy gaps as a function of average (a) MCI, (b) PDI, (c) I_{ring}, (d) FLU, (e) $NICS(0)_{zz}$, and (f) $NICS(1)_{zz}$ per ring for systems **1**, **3**, **5**, and **6** with n from 1 to 5. Solid and dashed lines correspond to singlet CS and the triplet values, respectively.

aromaticity of the triplet and CS states is minor and vice versa. Furthermore, it is important to mention that the T and OSS singlet states of CPHs are not 4N e^- Baird aromatic species as in the cyclopentadienyl cation but Hückel-type systems having 6π e^- per ring.

Figure 3 depicts the average aromaticity measures per ring. Depending on the number of rings and the symmetry and environment of these rings, we have defined four different ring types: A, B, C, and A′ (Figure 4a). A-type rings are located at the ends of the chain, and they are connected to two R groups on one side and another ring on the other side. B-type ones are surrounded by two other ring units but are not in the middle of the molecule. Finally, C and A′ type are in the center of the molecule with symmetric substitution but with the difference that C-type rings are in between two ring units whereas A′-type rings are in a terminal position.

Regarding the electronic aromaticity indices of each specific ring type, we observe that qualitatively MCI, PDI, I_{ring}, and FLU give the same results (see SI). The former four indices indicate that, as expected from resonance structures of Scheme 2, Chichibabin compounds are more aromatic in the T state than in the CS one, in which they are less aromatic (structures of type **II** provide some aromaticity, especially in the central rings) or are even nonaromatic, as can be seen for the case of A and A′ type of rings (Figure 4b). OSS structures are in between CS and T ones with n values from 3 to 5, and the difference between the OSS and T forms become less notable when n increases. The extra stabilization of the OSS comes from the quinoid resonance forms, which is not occurring in the case of the T. For this reason, the systems in the T state are more aromatic, as their unique structure is the benzoid form.

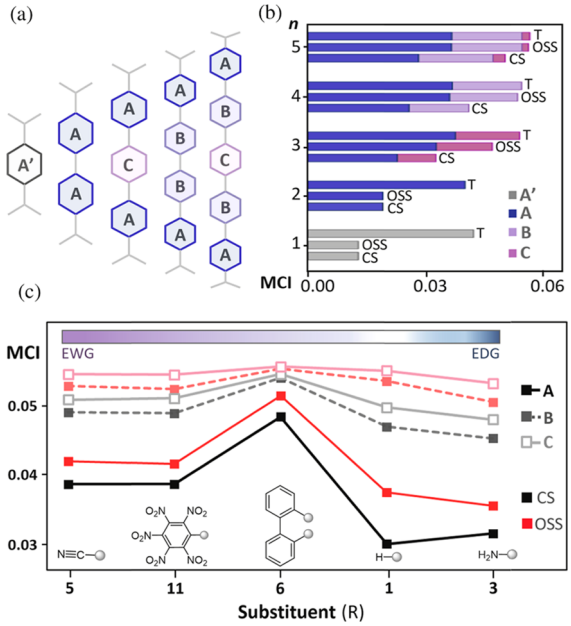

Figure 4. (a) Scheme of different ring types (A, A′, B, and C). MCI aromaticity indices (b) of A-, A′-, B-, and C-type rings for CS, OSS, and T states of system $\mathbf{1}_n$ with n = 1 to 5 and (c) of A-, B-, and C-type rings for CS and OSS states of the R = **1**, **3**, **5**, **6**, and **11** systems with n = 5.

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Figure 4b shows the behavior of the local aromaticity in $\mathbf{1}_n$ species, which is the general trend found in CPHs. First, the internal rings B and C are more aromatic than the terminal A and A′ ones. Second, there is an increase in the aromaticity of B and C rings with n in both singlet and triplet states. A-type rings show the same trend for CS and OSS states, but in the case of the T state, the increase of aromaticity with increasing n is not observed (Figure 4b).

Results in Figure 4c show that the terminal substituents have an influence on the aromaticity of the compounds, especially on the external rings. EWG favors the T and OSS states stabilizing the diradical character and increasing the aromaticity of the rings. It seems that the aromaticity decreases going from strong EWG as cyanide to strong EDG as amine, with the exception of aromatic substituents, which are poor EWG (the phenyl group has a weak π-donor and inductive withdrawing character) but present the largest aromaticity values. The latter family is especially good in stabilizing the radical forms because it can be delocalized over the π-system, which also explains why the R = aromatic are the systems with the most aromatic rings, especially the A-type ones. We can also observe that the differences between diverse substituted Chichibabin compounds are less noticeable in the central rings than in the external ones. The particular case of **11**, which has the most stable OSS and T state structures, does not present the high aromatic character that we would expect and the values obtained are similar to the ones of **5**.

The evaluation of the aromaticity by means of the NICS index leads to results similar to those yield by the electronic indices (see Tables S34−S36), as it was explained in the general comparison thereby referring to Figure 3. Nevertheless, there are differences when comparing individually the distinct types of rings. For the A type in the CS and OSS cases, the aromaticity increases going from small to large n values and from EDG to EWG. On the contrary, in the T state, the aromaticity decreases significantly when n increases. However, with the electronic indices, we observe that there was no variation in the aromaticity of A rings with changing n and with NICS we found meaningful changes. For example, compound $\mathbf{1}_n$ $\mathrm{NICS}(0)_{zz}$ values for n = 1−5 are −3.3, −0.3, 1.8, 2.7, and 2.8. In B-type rings, the aromaticity increases with n for the OSS and CS, and it is maintained for the T. Finally, for C-type rings, the aromaticity increases when increasing n in all cases. It is likely that this particular behavior of the NICS indicator of aromaticity is caused by the coupling of the magnetic fields generated by neighboring rings.[51−53]

■ CONCLUSIONS

The molecular and electronic structures of Chichibabin's polycyclic hydrocarbons have been studied to discuss the effects of elongating the π-system and changing the exocyclic substituents. For large n systems, an increase of the twisting distortion is observed as a consequence of the H···H biphenyl-like repulsions, leading to a loss of planarity and conjugation. All CPHs systems present singlet−triplet energy gaps lower than 1.4 eV. Among them, most of the systems with $n > 2$ have small ΔE_{ST} ranging from 200 to 0.2 meV, thus being potential candidates for the design of new materials with NLO properties. The resonance structures proposed, together with the fact that the energy difference between OSS and the triplet is reduced when the distance between radical centers increases, gives a good explanation for the lowering of the ΔE_{ST} when going from n = 1 to 5. Species $\mathbf{1}_3$, $\mathbf{4}_3$, $\mathbf{5}_3$, and $\mathbf{6}_2$ have almost degenerated CS and T states (with energy differences lower than 0.03 eV), whereas almost all systems with n = 5 as well as $\mathbf{11}_3$ and $\mathbf{11}_4$ have particularly stable diradical GS. The aromaticity measures show a gain of aromaticity with the increase of n. Central B and C rings are more aromatic than external A-type rings. Aromatic substituents and EWG tend to stabilize the diradical(oid) forms better than EDG. These findings help in understanding the effect of exocyclic substituents and π-system length on ΔE_{ST} values of Chichibabin diradical(oid)s and may aid in the design of tuned π-electron materials for molecular electronics.

■ COMPUTATIONAL DETAILS

All geometry optimization, energy, and nucleus-independent chemical shift (NICS) calculations were performed with the Gaussian16 set of programs.[54] To select an appropriate method for the calculations, several DFT functionals were tested and compared against CCSD(T)/cc-pVDZ//QCISD-(T)/cc-pVXZ (X = D, T) results for the R = H and n = 1 and 2 systems (see Tables S1−S3 in the SI). As a result of this test and also based on some calculations of spin-state splittings found in the literature,[55−60] we conclude that the best option for these systems is to use the OPBE/cc-pVTZ level of theory.[61,62] In addition, for *meta*- and *para*-benzyne, it was shown that pure generalized gradient approximation functionals such as OPBE were superior to hybrid functionals for the description of the open-shell singlet state.[63−65] Moreover, for systems $\mathbf{1}_{1-5}$, we compared the OPBE and the range-separated LC-OPBE and ωB97xD results to see how long-range corrections affect the description of the systems with large n values (3−5). The range-separated functionals give larger spin contamination values, with $\langle \hat{S}^2 \rangle$ between 1.2 and 1.8 for the case of OSS and more than 2 for T (see Table S4 of SI). In the case of OSS systems, we perform broken-symmetry calculations giving as a result the collapse on CS species in the cases of $n \leq 2$ and OSS structures in the other cases. We have taken a pragmatic approach and have not applied spin contamination corrections for three reasons: (i) the concept of spin contamination is not completely meaningful at the DFT level because of the absence of a strict definition of the wave function;[66] (ii) when the overlap between open-shell orbitals is small, errors due to spin contamination are minor;[67] and (iii) for benzyne isomers, spin contamination corrections to DFT results lead to worse predictions of ΔE_{ST} as compared to experimental results.[68] We have checked the stability of the approximated DFT wave function for all species. The diradical character (y) of the OS systems has been estimated making use of the spin-unrestricted natural orbitals (UNOs) with the following index proposed by Kamada et al.[69−71]

$$y = \frac{(1 - T)^2}{1 + T^2} \text{ and } T = \frac{n_{\mathrm{HOMO}} - n_{\mathrm{LUMO}}}{2} \quad (1)$$

where n_{HOMO} and n_{LUMO} are the occupation numbers of the bonding and antibonding UNOs.

The aromaticity of the electronic structures was studied using geometric (HOMA),[45−47] electronic[72] (PDI,[73] I_{ring},[74] FLU,[75] and MCI[76]), and magnetic (NICS) aromaticity indices.[77,78] For the latter, we have evaluated three positions of the space NICS (0, 1, and −1) (shown in Figure S5 of SI). The aromaticity indices (except for NICS, which has been calculated with Gaussian16) have been computed using AIMall[79] together with ESI-3D packages.[75,80,81]

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00916.

More detailed computational procedures; analysis of the conformers; and complete aromaticity results, y values, spin densities, and energy results (PDF)

Coordinates of the OPBE/cc-pVTZ optimized geometries (XYZ)

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Notes

The authors declare no competing financial interest.

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